

Indirect cathodic reduction of dispersed indigo by 1,2-dihydroxy-9,10-anthraquinone-3-sulphonate (Alizarin Red S)

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Abstract The indirect cathodic reduction of dispersed indigo (Vat Blue 1) with 1,2-dihydroxy-9,10-anthraquinone-3-sulphonate (Alizarin Red S) as soluble mediator system was studied in 0.1 M NaOH by cyclic voltammetry, voltammetry in a flow cell and in galvanostatic reduction experiments. In cyclic voltammetry, the presence of 17.1 mM indigo led to an increase in the diffusion-controlled cathodic peak current ($I_{p,d}$) by a factor of 2. During the reverse scan of the voltammograms the oxidation of reduced indigo could be observed at -650 mV (vs. Ag/AgCl, 3 M KCl). In voltammograms of 4.0 mM ALS in 0.1 M NaOH, recorded in a flow cell, a current density of 0.40 – 0.46 mA cm $^{-2}$ was determined for the diffusion-controlled cathodic current plateau, which appeared in the potential range of -850 to $-1,050$ mV. In galvanostatic batch electrolysis, solutions containing 2.5–3.8 mM reduced indigo were prepared and analysed by spectrophotometry and tested in dyeing experiments. The dyeing behaviour of the reduced indigo was independent of the reduction technique used. Energy consumption for electrochemical reduction of 1 kg of indigo could be estimated to 6.5 kWh kg $^{-1}$.

Keywords Indigo · Vat Blue 1 · Vat dye · Cyclic voltammetry · Alizarin Red S · Indirect electrolysis

Introduction

In the coloration of cellulosic textiles, vat dyes represent a class of colourants, which offers particularly high level of quality. Indigo (Vat Blue 1) also belongs to this class of dyes; however, it is used as single dye for a special market, the production of denim fabric for jeans. The annual production of indigo dyed denim fabric can be estimated with 3 billion linear metres [1].

As a characteristic step of their application, vat dyes require the use of reducing agents to form their alkali soluble leuco-dye, which exhibits affinity to the cellulose substrate [2]. At present the technically applied reducing agents cannot be regenerated and their disposal into the wastewater causes considerable ecological problems. Representative examples for reducing agents for vat dyes are dithionite, hydroxyacetone, sodium borohydride, formaldehyde sulphonylates and glucose [3–5].

Reversible redox couples with sufficiently negative redox potential could be used as reducing agents, which can be regenerated electrochemically [6–10]. For the indirect cathodic reduction of vat dyes different chemical principles have been proposed in the literature, which either base on the use of alkali-stable iron complexes or anthraquinoid compounds [11–15].

In the literature, studies describing the electrochemical properties of alkali soluble anthraquinoid compounds have been reported [16–26]. A detailed analysis of the electrochemical properties of different dihydroxy-anthraquinones by cyclic voltammetry indicated substantial potential 1,2-dihydroxy-9,10-anthraquinone-3-sulphonate (Alizarin Red S, ALS) as possible mediator [27]. Vat dyes require a reduction potential of -900 to $-1,000$ mV (vs. Ag/AgCl, 3 M KCl reference electrode), thus the more powerful iron–amino complexes or iron–gluconate complexes are suited

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better for this application. The reduction potential of ALS near -800 mV limits a possible application to dyestuff systems with lower redox potential for examples indigo (-700 mV) or sulphur dyes (-600 mV) [5, 28–30].

The direct cathodic reduction of indigo mechanically immobilised on the surface of a graphite electrode has been studied by voltammetry [31, 32]. The redox behaviour of the indigo/leuco-indigo couple also has been investigated by voltammetry using a mercury electrode [33].

At present only very limited information about the electrochemical behaviour of the system ALS–vat dye has been published in the literature [27, 34]. In particular, information about the behaviour of ALS in electrochemical indigo reduction is not available.

In this study, the electrochemical behaviour of the system ALS/dispersed indigo has been studied by cyclic voltammetry, voltammetry in a flow cell and batch electrolysis. Voltammograms of ALS and ALS in presence of dispersed indigo were recorded in a flow cell to characterise the electrochemical behaviour of ALS in alkaline solution. Reduction experiments using a multi-cathode electrolyser were performed to prepare reduced indigo in sufficient amount to undertake dyeing tests. Dyeing characteristics of the reduced leuco-indigo solution were studied, to identify possible changes in dyestuff behaviour and final colour of the dyeing.

Experimental

Materials

The 1,2-dihydroxy-9,10-anthraquinone-3-sulphonate (Alizarin Red S) was used as delivered by the supplier (Riedl-de-Haen, Seelze, Germany). Analytical grade NaOH was used for the electrochemical experiments. Technical grade citric acid, NaOH, FeCl_2 , triethanolamine (TEA), indigo (CI Vat Blue 1, DyStar Indigo[®] gran.) and hydrogenated indigo solution (CI Leuco Vat Blue 1, DyStar Indigo Vat Solution[®]) both from DyStar Textilfarben, Frankfurt a. M., Germany, were used for determination of indigo concentration, electrochemical and dyeing experiments. Desized, scoured and bleached cotton fabric was used for dyeing experiments (Getzner Textil AG, Bludenz, Austria).

Cyclic voltammetry

Cyclic voltammetric experiments were carried out employing a three-electrode configuration. The apparatus used for the experiments was an EG&G 264 A Potentiostat with a 303A HMDE (small drop size, drop area 0.96×10^{-2} cm²). A platinum wire served as counter electrode. The cyclic

voltammograms were recorded on a Rikadenki X-Y recorder. All potentials given were measured vs. a (Ag/AgCl, 3 M KCl) reference electrode. The test solutions were aerated for 8 min with He/Ar (inert gas) to eliminate interfering oxygen. All experiments were performed at room temperature.

Preparation of indigo dispersion

For preparation of the indigo dispersion, a defined volume of leuco-indigo solution was air oxidised in 0.1 M NaOH by stirring overnight in a beaker. For the CV experiments in presence of dispersed indigo, the dispersion was added to a solution of ALS in 0.1 M NaOH. The photometric determination of the indigo concentration was performed by reduction of the dispersed indigo dye into its soluble yellow leuco form, by addition of the Fe(II)–TEA complex to a defined volume of sample [35]. A solution of the composition 0.144 M FeCl_2 , 1.71 M TEA, 0.0042 M citric acid and 0.825 M NaOH served as reducing agent. The absorbance of the reduced indigo then was measured at 405 nm (1-mm flow-through cuvette, single-beam filter photometer Merck SQ 300). Calibration curve was prepared based on solid indigo (DyStar Indigo gran., Frankfurt a.M., Germany).

Photometry of ALS as function of pH

To record the absorbance spectra of ALS as function of pH, a 5-mM ALS solution was prepared. One hundred millilitres of solution were acidified with 10 ml 0.05 M HCl. The absorbance of the solution was measured by circulating the solution through a flow-through cuvette with 0.1 mm path-length (Zeiss CLH 500/MCS521 UV-vis, Carl Zeiss (Jena) Germany). Then the solution pH was increased stepwise by addition of 1 M NaOH solution. pH measurement of the electrolyte was made with a glass electrode and a potentiometer (Hamilton-flush-trode, Orion 720 A, Boston, MA, USA)

Adsorption of ALS on dispersed indigo

To study the absorption of ALS on dispersed indigo in alkaline aqueous solution, a dispersion of indigo was prepared by air oxidation of leuco-indigo solution in 0.1 M NaOH. The concentration of dispersed indigo was determined by photometry of the indigo after reduction into the alkali soluble leuco-indigo form at a wavelength of 405 nm. By this method a dispersion with an indigo content of 34 mM (8.97 g L^{-1}) indigo was prepared. A volume of 50 ml indigo dispersion then was mixed with different volumes of 5 mM ALS solution in 0.1 M NaOH and filled to 100 ml with 0.1 M NaOH. The solutions were

characterised by CV experiments in the potential range of -200 to $-1,000$ mV.

For comparison ALS solutions without dispersed indigo were studied. Before the absorbance of ALS was measured, dispersed indigo particles were removed by filtration through a $0.2\text{-}\mu\text{m}$ membrane filter (VWR International, Vienna, Austria). The absorbance of the filtered ALS solution was compared to ALS solutions of the same composition (Zeiss CLH 500/MCS 521 UV-VIS, Carl Zeiss Jena, Jena, Germany, 10 mm cuvette). The absorbance of soluble compounds present in the leuco-indigo solution was determined using an indigo dispersion without addition of ALS. After removal of the dispersed indigo the absorbance of the filtrate at 556 nm used for correction of the absorbance of the filtered ALS samples.

Voltammograms in a flow cell

All experiments were recorded at ambient temperature. The voltammograms were measured in a flow cell with parallel plate geometry [36]. The catholyte and anolyte were separated by a cation exchange membrane (Nafion type). A Cu cathode with 100 cm^2 area was used (Cu-foil, Merck, Darmstadt, Germany). The anode was made from stainless steel. The catholyte was circulated by a peristaltic pump through the catholyte compartment with a flow of 140 ml min^{-1} , which corresponds to an estimated average catholyte flow in the cell of $0.15\text{--}0.20\text{ cm s}^{-1}$. Total volume of catholyte was 800 ml . Four hundred millilitres of 1 M NaOH were used as anolyte. In the catholyte 0.1 M NaOH was used as ground electrolyte. The cell voltage was adjusted by means of an adjustable power supply. All potential values are given related to a (Ag/AgCl, 3 M KCl) reference electrode and were measured using a potentiometer (Metrohm pH metre 654, Fa. Metrohm, Herisau, Switzerland). The voltammograms were recorded by stepwise adjustment of the cathode potential and registration of the cell current.

Batch electrolysis experiments—construction of the electrochemical cell

A multi-cathode cell was used for dyestuff/dyebath reduction [36]. Three cathodes were driven by separately adjustable electric power supplies, connected to a common anode. Catholyte and anolyte were separated by a cation exchange membrane (Nafion[®]). A solution of 1 M NaOH was used as anolyte and a stainless steel electrode (front area 100 cm^2 , V4A-stainless steel) served as anode. The cathodes were three-dimensional electrodes manufactured from stainless steel fabric (steel 1.4404, aperture size 0.325 mm , wire diameter: 0.2 mm , open area 37%; Haver

and Boecker, Oelde, Germany), each cathode unit exhibiting a front area of 100 cm^2 and surface area of $1,440\text{ cm}^2$, thus giving a full cathode area of $4,320\text{ cm}^2$. The cathode units were insulated from each other by three layers of PE fabric. The catholyte circulation through the electrode was driven by a peristaltic pump which was adjusted at 140 mL min^{-1} . Assuming equal flow and a porosity of 40% in the cathodes, the average catholyte velocity through the electrodes can be calculated as 0.06 cm s^{-1} . The volume of the catholyte was $750\text{--}1,000\text{ ml}$ and the anolyte volume was 350 ml . Temperature and redox potential were measured in the dyebath (Metrohm pH metre 654, Metrohm, Herisau, Switzerland). All potential values given are related to the (Ag/AgCl, 3 M KCl) reference electrode. Each of the three cathodes was supplied by a constant current of 0.5 A . The change in absorbance was measured by means of a diode array spectrophotometer (Zeiss CLH 500/MCS 521 UV-VIS, Carl Zeiss Jena, Jena Germany) using a 0.1-mm flow-through cuvette.

To simulate technical conditions, the experiments were not performed under inert atmosphere. The concentration of ALS was 3.12 mM . NaOH (0.1 M) served as ground electrolyte for the experiment at pH 13. In the electrolysis experiment at pH 11.5–12.0 5.4 mM NaOH was used and the raise in pH was compensated by addition of technical grade acetic acid. To avoid formation of Ca^{2+} -ALS complexes 1 ml L^{-1} NTA-based complexing agent (nitrilo-triacetic-acid-sodium salt, Trilon TA liq., BASF Ludwigshafen, Germany) was added. After the reduction experiment the catholyte was oxidised by stirring in an open beaker overnight and the absorbance of the oxidised solution was measured. In batch electrolysis experiments, the ALS containing catholyte was reduced to achieve a redox potential of -800 mV , then a defined amount of indigo was added and the duration to reach the same potential as before addition was recorded. From the charge flow and the amount of indigo added, the overall current efficiency of the system was calculated. After full dyestuff reduction was achieved, the catholyte was used for dyeing experiments.

Dyeing experiments

The fabric samples were immersed into the reduced indigo bath for approximately 15 s . Excess dyebath was stripped off by means of two glass rods and the sample was oxidised in air for 120 s . On the same sample the dyeing procedure was repeated up to four times, to study the build up of indigo dyestuff. A $40\text{ }^\circ\text{C}$ washing bath containing 10 ml L^{-1} complexing agent (Trilon TA, nitrilo-triacetic-acid-sodium salt) was required to avoid any Ca^{2+} -ALS complex formation on the fabric. Finally, the samples were rinsed in deionised water.

Colour coordinates (CIELab values) and K/S values were determined with a Konica Minolta Spectrophotometer CM-

3610d (10° observer). Colours are given in CIELab coordinates, L^* corresponding to the brightness (100 = white, 0 = black), a^* to the red–green coordinate (positive sign = red, negative sign = green) and b^* to the yellow–blue coordinate (positive sign = yellow, negative sign = blue).

Dyestuff content on the dyed fabric was determined according the Kubelka-Munk function, the K/S values were calculated from the reflectance β determined at 660 nm according $K/S=(1-\beta)^2/2\beta$.

Results and discussion

Cyclic voltammetry

The indirect reduction of dispersed indigo by ALS was characterised by cyclic voltammetry. As function of pH dissociation of the phenolic hydroxyl groups in the ALS can occur. Due to the presence of two phenolic hydroxyl groups ALS shows pH-dependent deprotonation with change of colour [37, 38].

The absorbance spectra of a 5 mM ALS solution as function of solution pH are given in Fig. 1. As can be seen, dependent on the pH of the solution, three different species are present in solution: under acidic conditions the dihydroxy-sulphonate form $ALSH_2$, bearing two non-dissociated hydroxyl groups, prevails. At pH 8, one hydroxyl group is present in dissociated form ($ALSH^-$) and at pH 12.5 both phenolic hydroxyl groups are present in their phenolate form (Eqs. 1 and 2).

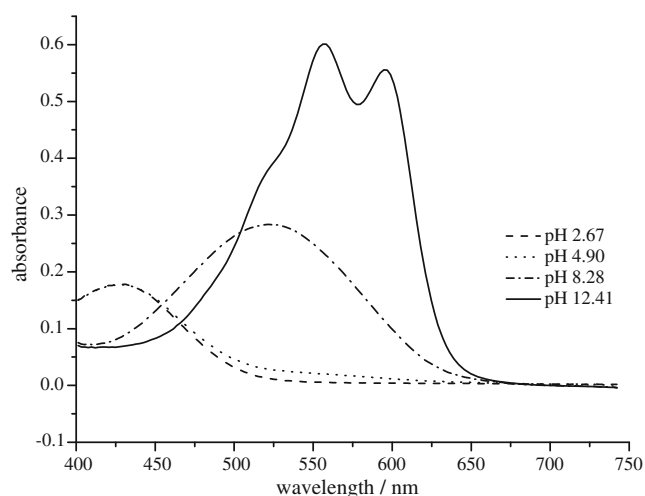
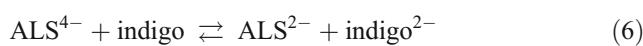
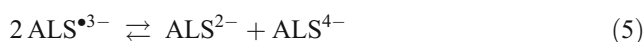


Fig. 1 Change in absorbance of a 5 mM ALS solution at different pH values (broken line) pH 2.67; (dotted line) pH 4.90; (dashed-dotted line) pH 8.28; (line) pH 12.41

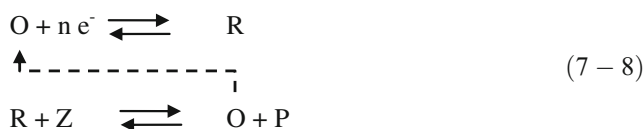
The CV experiments with ALS were performed at a NaOH concentration of 0.1 M, thus both phenolic hydroxyl groups are full dissociated and ALS^{2-} is the electroactive species present in solution.

At pH 12–13, ALS^{2-} represents the oxidised species and becomes reduced by cathodic electron transfer to ALS^{4-} . In a simplified representation, the reduction of ALS^{2-} follows Eqs. 3 to 6. The reduction of an ALS^{2-} proceeds via a consecutive series of two rapid one electron transfer reactions according Eqs. 3 and 4. In aqueous solution the formation of the radical anion is not observed and steps (3) and (4) both proceed as two electron transfer reaction with formation of an ALS^{4-} ion. Formation of ALS^{4-} can result from transfer of a second electron to the radical anion (Eq. 4) or from disproportionation of the radical anion according Eq. 5 [16–21].



Dispersed indigo dye then is reduced by ALS^{4-} according Eq. 6 and the oxidised form of the ALS^{2-} is regenerated. Also protonation of the ALS^{4-} can occur, dependent on solution pH.

Under the conditions studied dispersed indigo is not electrochemically active. Thus in presence of dispersed indigo dye, the reaction scheme is similar to an electrode reaction with catalytic regeneration of the oxidised component (Eqs. 7 and 8) [39]. In Eqs. 7 and 8, O and R represent ALS^{2-} and ALS^{4-} , respectively. Z corresponds to the oxidised form of indigo and P stands for the reduced leuco-indigo.



Indigo is present in dispersed oxidised form, thus an application of theoretical models for homogeneous catalytic reactions in cyclic voltammetry is difficult. A simplified description of the catalytic performance of a mediator system can be achieved by enhancement factors $e.f. = (I_p)_c / (I_p)_d$ [40]. The reduced indigo dye dissolves in the alkaline medium and is oxidised during the anodic scan of the CV experiment. Thus the anodic current, which can be

attributed to this oxidation step, can also be used to assess a mediator system.

Figure 2 shows the cyclic voltammogram of 2 mM ALS²⁻ in 0.1 M NaOH and the same voltammogram in presence of 17.1 mM dispersed indigo.

The presence of reducible dispersed dyestuff leads to an increase of (*I*_p)_d, the diffusion-controlled cathodic peak current, to (*I*_p)_c, the catalytic cathodic peak current. A representative example for voltammograms of ALS in presence of dispersed indigo at scan rates between 5 and 50 mV s⁻¹ is shown in Fig. 3.

In Fig. 4, the so-called enhancement factors (*I*_p)_c/*I*_p)_d of 0.5–2.5 mM ALS in presence of 17.1 mM indigo are given as function of scan rate. The decrease in *e.f.* with increasing scan rate is due to the decoupling of the cathodic reduction of ALS from the catalytic reaction. At 2.5 mM ALS and low scan rates of 5–20 mV s⁻¹ *e.f.* decrease. At this conditions, the assumption of a high excess in indigo concentration over the ALS concentration, required for quasi-stationary conditions, is no more valid.

As the reduced ALS⁴⁻ reacts with the dispersed indigo, during the reverse scan of the voltammogram, the oxidation of reduced indigo is observed at a potential near -650 mV instead of the oxidation of ALS⁴⁻ (Fig. 3). The anodic current peak (*I*_p)_a for reoxidation of reduced indigo does not exhibit linear behaviour against the square root of scan rate. Particularly at lower concentration of ALS the increase of (*I*_p)_a with square root of scan rate is not linear (Fig. 5). This behaviour can be explained by two reasons, at first the assumption of electrochemical reversibility for the indigo oxidation is not valid and at second at high scan rates of 100 mV s⁻¹ the limited reaction rate between ALS⁴⁻ and dispersed indigo begins to determine the concentration of leuco-indigo formed.

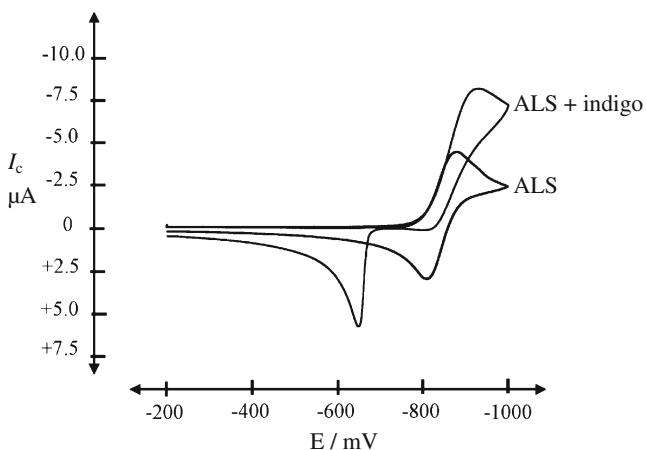


Fig. 2 Cyclic voltammogram of 2.0 mM ALS²⁻ in 0.1 M NaOH at a scan rate 50 mV s⁻¹ and experiment in presence of 17.1 mM indigo

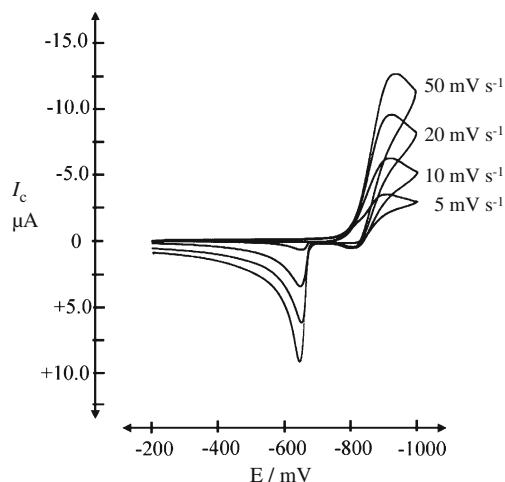


Fig. 3 Cyclic voltammogram of 2.54 mM ALS in presence of 17.1 mM indigo in 0.1 M NaOH as function of scan rate (5, 10, 20 and 50 mV s⁻¹)

Voltammograms in a flow cell

To study the electrochemical behaviour of the system indigo/ALS at larger scale voltammograms in a divided 100 cm² parallel plate cell were recorded. The voltammograms of 2.0, 3.9 and 5.9 mM ALS and of the ground electrolyte are shown in Fig. 6.

Below -450 mV (vs. Ag/AgCl, 3 M KCl) dissolved oxygen is reduced at the cathode. Between -200 mV and -750 mV no significant differences in current density between ALS solutions and ground electrolyte are observed. The cathodic reduction of ALS begins at potentials below -800 mV. At the beginning of the diffusion-limited current plateau, a current peak is observed, which can be explained with the reduction of the Cu-ALS complex formed at the surface of the copper cathode [41]. In the potential interval of -850 to -1,050 mV, the increase in current density is proportional to the ALS concentration.

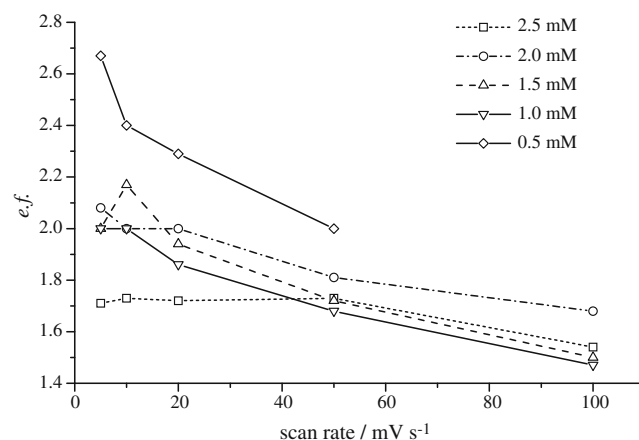


Fig. 4 *e.f.* of 0.5–2.5 mM ALS in presence of 17.1 mM indigo dispersion in 0.1 M NaOH

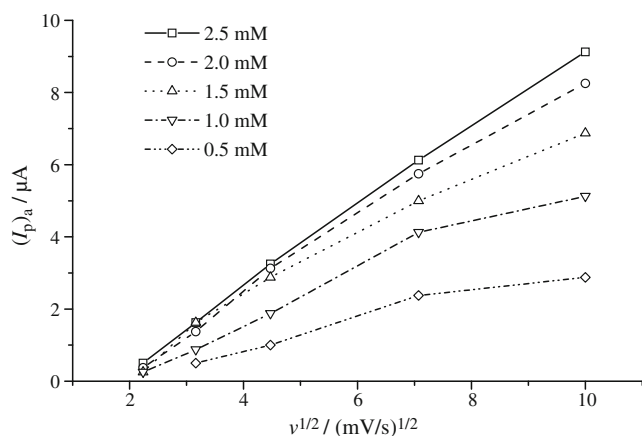


Fig. 5 Anodic current peak $(I_p)_a$ for reoxidation of indigo as function of square root of scan rate (0.5–2.5 mM ALS in presence of 17.1 mM indigo dispersion in 0.1 M NaOH)

For a 5.9 mM ALS solution in 0.1 M NaOH, the diffusion-limited cathodic current plateau is observed at a current density of around 0.55 mA cm^{-2} at an average catholyte velocity of $0.15\text{--}0.2 \text{ cm s}^{-1}$.

In another experiment, the cathode potential was maintained at -250 mV to prevent surface oxidation and Cu–ALS complex formation. As can be seen in Fig. 7, similar voltammograms of the ALS solution were recorded and a cathode potential of -225 to -275 mV was found insufficient to prevent Cu–ALS complex formation at the cathode surface. A visible control of the Cu cathode after the experiments showed slight colour change most probably due to formation of insoluble species on the surface.

The formation of oxidised species at the cathode surface could be stopped with a constant cathodic current of 2 mA , which was maintained between the voltammograms. This current corresponds to a current density of 0.02 mA cm^{-2} .

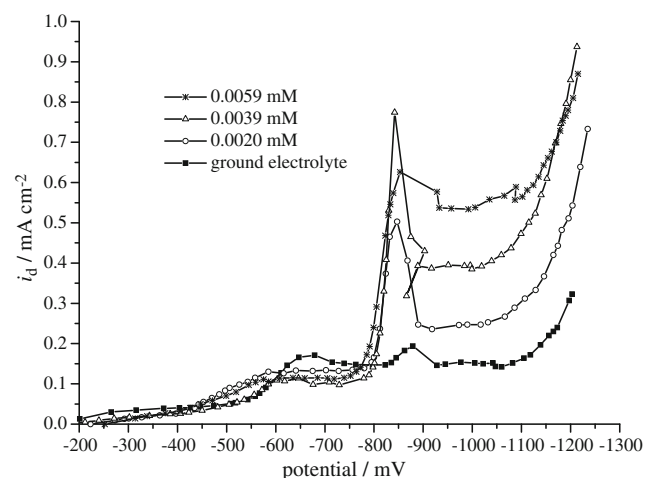


Fig. 6 Voltammograms of (close square) ground electrolyte (open circle) 2.0, (open triangle) 3.9, (asterisks) 5.9 mM ALS in 0.1 M NaOH recorded in the flow cell

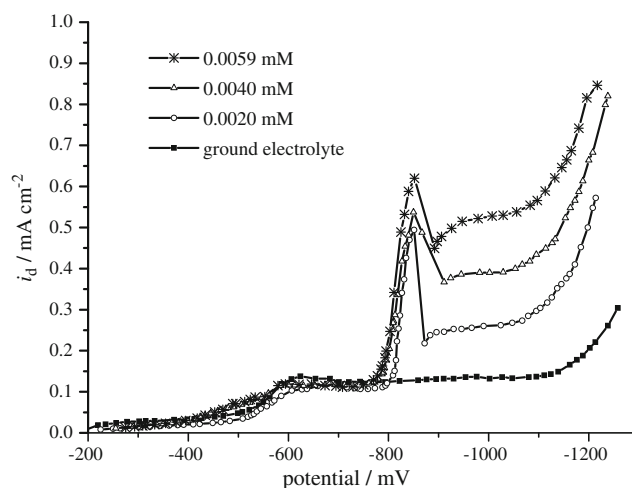


Fig. 7 Voltammograms of (close square) ground electrolyte and (open circle) 2.0, (open triangle) 4.0, (asterisks) 5.9 mM ALS in 0.1 M NaOH. Between experiments cathode potential was maintained at -225 to -275 mV

In the voltammograms the cathodic peak near -800 mV disappeared and a clean cathode surface was obtained at the end of the experiments.

To study the indirect cathodic reduction of dispersed indigo, voltammograms of dispersed indigo, were recorded before and after addition of ALS. Two concentrations of dispersed indigo, 2.44 mM (0.64 g L^{-1}) indigo and 9.81 mM (2.57 g L^{-1}) indigo, were studied. NaOH (0.1 M) was used as ground electrolyte and a concentration of 4.0 mM ALS was used as mediator system. No indication of direct cathodic indigo reduction was observed in the voltammograms of dispersed indigo in NaOH solution. The reduction of ALS can be observed in the potential range between -850 and $-1,050 \text{ mV}$. The diffusion-limited cathodic current plateau of a 4.0 mM ALS solution in presence of 2.44 mM (0.644 g L^{-1}) indigo was measured with $i_d = 0.46 \text{ mA cm}^{-2}$ (Fig. 8).

The 4.0 mM ALS solution reached 0.40 mA cm^{-2} (Figs. 6 and 7). An increase of concentration of dispersed indigo from 2.44 mM (0.64 g L^{-1}) to 9.81 mM (2.57 g L^{-1}) did not result in an increase in diffusion-limited current density. At 9.81 mM indigo an i_d of 0.36 mA cm^{-2} is observed, which is comparable to the diffusion-limited current plateau of ALS alone. In the literature, the influence of dispersed indigo on the diffusion-limited plateau of the Fe–triethanolamine complexes in strongly alkaline solution has been reported. The increase of i_d with indigo concentration however was much less than expected from the *ef.* measured in CV experiments [42]. The limited influence of dispersed indigo on current density in flow cells is due to the low diffusion rate of the dispersed particles into the hydrodynamic boundary layer of the electrode. Thus after the indigo particles initially present in the diffusion layer have been reduced, the concentration profile of ALS and

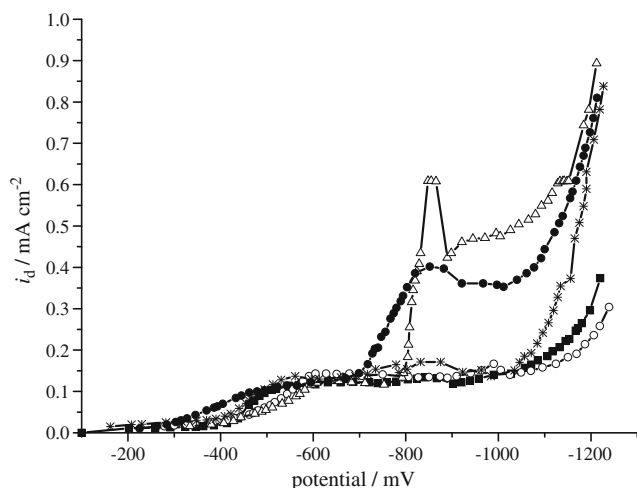


Fig. 8 Voltammogram 2.44 mM (0.64 g L^{-1}) and 9.81 mM (2.57 g L^{-1}) dispersed indigo in 0.1 M NaOH and in presence of 4.0 mM ALS. (*close square*) 0.025 M NaOH, 2.44 mM indigo; (*open circle*) 0.1 M NaOH, 2.44 mM indigo; (*asterisks*) 0.1 M NaOH, 9.81 mM indigo; (*open triangle*) 0.1 M NaOH, 2.44 mM indigo, 5.0 mM ALS; (*close circle*) 0.1 M NaOH, 9.81 mM indigo, 5.0 mM ALS

ALS^{2-} in the hydrodynamic boundary layer is almost independent on the presence of dispersed indigo in the bulk solution.

Adsorption of ALS on dispersed indigo

To study possible adsorption of ALS on dispersed indigo a series of photometric experiments was performed. An ALS solution of known concentration was mixed with a dispersion of freshly prepared oxidised indigo to obtain a solution containing 0.5–2.5 mM ALS and 17.1 mM dispersed indigo. After removal of the dispersed indigo, the absorbance was measured at 556 nm and compared to a solution of ALS.

In Fig. 9, the absorbance at 556 nm of ALS solutions and filtered indigo/ALS solutions are shown as function of initial ALS concentration.

In presence of dispersed indigo the absorbance of the filtered ALS solution decreased approximately 5% to 10%, which can be explained with adsorption of dissolved ALS on the surface of dispersed indigo particles. Part of the ALS adsorbs on the dispersed indigo, thus the effective concentration of electroactive species decreases. As a result a decrease of i_d in presence of dispersed indigo can occur (Fig. 8). Further investigations would be required to analyse the system in more detail, which however is beyond the scope of the present study.

Galvanostatic electrolysis experiments

To study the indirect reduction of indigo in batch electrolysis experiments, galvanostatic electrolysis experi-

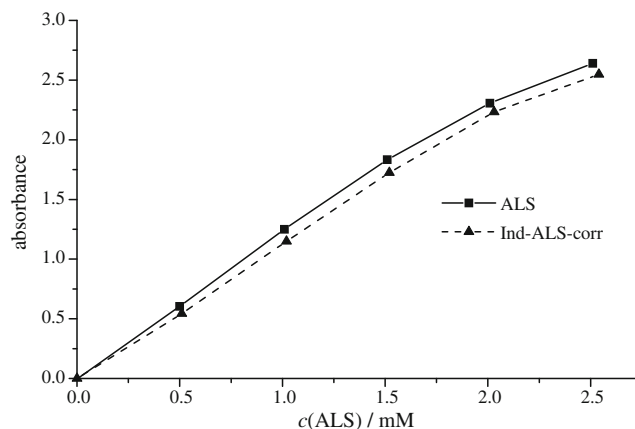


Fig. 9 Absorbance measured at 556 nm of (*close square*) ALS solutions and (*close triangle*) filtered 17.1 mM indigo/ALS mixtures, as function of ALS concentration

ments were performed at different pH, using a multi-cathode electrolyser. Both ALS and indigo exhibit different colour in oxidised and reduced state, e.g. the blue indigo dispersion changes into a yellow solution of reduced indigo, thus the reduction of ALS and of indigo can be monitored by photometry. In a first experiment, the cathodic reduction of ALS and the reduction of dispersed indigo were followed by photometry. The experiment was performed at pH 12.7–13.0, at a temperature between 21 and 24 °C. The three cathodes were supplied with 0.5 A current each. During electrolysis, cell voltage decreased from initially 4.6 V for the first cathode and 6.1 V for the third electrode, to 3.7 V and 4.0 V respectively, measured at the end of the electrolysis. A volume of 0.750 L was electrolysed for 230 min. The redox potential in solution decreased from initially -371 to -889 mV. Oxidised indigo

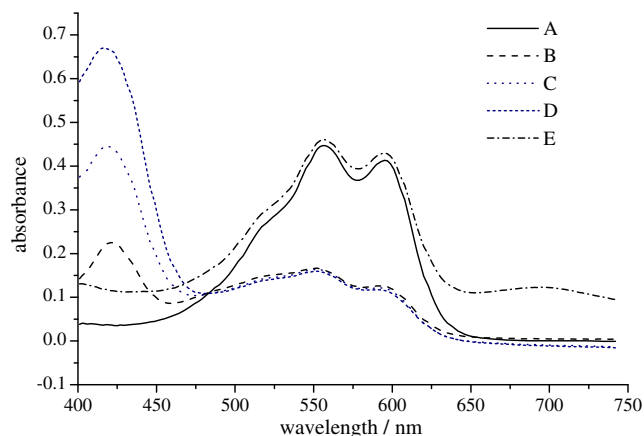


Fig. 10 Photometric curves registered during cathodic reduction experiment of ALS and indigo in 0.1 M NaOH. (*line*) A initial solution with oxidised ALS^{2-} , (*dashed line*) B reduced ALS^{4-} at -882 mV, (*light dotted line*) C first addition of indigo, fully reduced at -885 mV, (*dark dotted line*) D second addition of indigo, fully reduced at -889 mV, (*dashed-dotted line*) E oxidised catholyte containing ALS^{2-} and indigo at -79 mV

Table 1 Experimental results of batch electrolysis experiments at pH 13

	Time min	I_1-I_3 A	U_{z1} V	U_{z2} V	U_{z3} V	E mV	T °C	η %	Comments
	0	0.503	4.47	4.58	4.86	0	21		
	15	0.503	4.62	4.73	5.75	-764	22		
	20	0.503	4.62	4.73	5.75	-801	22	18	Addition of indigo 0.5273 g
	50	0.502	4.23	4.33	5.11	-811	-	20	Addition of indigo 0.5188 g
I_1-I_3 individual cathode current	70	0.502	4.09	4.19	4.91	-819	23		Sample 1
cathode 1–3, $U_{z1}-U_{z3}$ cell	75	0.502	4.09	4.19	4.91	-828	23		Sample 2
voltage, E redox potential in	80	0.502	4.09	4.19	4.91	-837	23		Sample 3
catholyte, pH and temperature T ,	90	0.502	4.09	4.19	4.91	-846	-		Sample 4
η current efficiency, time of	100	0.502	3.78	3.86	4.14	-882	24		
indigo addition and dyeing									
experiments									

was added in two portions of 1 mmole after a potential below -880 to -885 mV had been reached, thus the total concentration of indigo at the end of the electrolysis was 2.58 mM. At the end of the electrolysis, the catholyte was stirred overnight and the absorbance of the oxidised solution was recorded. The photometric results of the initial ALS solution, the same solution at a redox potential of -882 mV, after addition of indigo and the oxidised solution are shown in Fig. 10.

At the beginning of the electrolysis, the absorbance spectrum indicates the presence of oxidised ALS²⁻. With cathodic reduction of ALS²⁻, the absorbance maxima at 555 and 595 nm decrease and a new maximum corresponding to ALS⁴⁻ appears at 420 nm. Following to the addition of indigo the formation of leuco-indigo can be monitored at 415 nm. The reduced dye bath, containing ALS⁴⁻ and dissolved leuco-indigo, exhibits strong absorbance at 425 nm and small peaks at 555 and 595 nm.

After oxidation of the reduced indigo and ALS⁴⁻, the two maxima at 555 and 595 nm reappear again. The formation of insoluble blue indigo pigment can be seen in a general increase of the baseline due to presence of dispersed particles, with a maximum absorbance at 695 nm.

The current efficiency achieved in batch reduction experiments was determined at pH 13 (0.1 M NaOH) and

at pH 11.6–12.0 (5.4 mM NaOH). After a negative redox potential of approximately -800 mV had been reached, oxidised indigo was added to the catholyte. During the time of indigo reduction, more positive potentials are observed and the same negative potential is reached first after complete indigo reduction has been achieved. Thus from the time required to reach the same catholyte potential, as before the addition of indigo, the current efficiency η for indirect cathodic reduction of indigo can be calculated. Experimental data are given in Tables 1 and 2.

At pH 13, a total current yield of 18–20% is observed, which decreases to 9–11% at pH 11.8–12. Also the time to build up a redox potential of -800 mV differs between the two experiments. At pH 12, a time of 195 min (charge flow 5 Ah) is required to reach -800 mV, while at pH 13 20 min electrolysis (charge flow 0.5 Ah) are sufficient to build up a reduction potential of -800 mV. The conditions of the electrolysis have not been optimised, thus increased current efficiency can be expected under optimised conditions. Repetition of the electrolysis experiment at pH 13 under Ar-atmosphere did not result in a significant improvement of the current yield of 20%, thus the oxidative load, due to presence of air oxygen, is comparably low.

At pH 11.8–12, a lower amount of electrolyte is present in the catholyte. Particularly in the initial phase of the

Table 2 Experimental results of batch electrolysis experiments at pH 11.6–12.0

	Time min	I_1-I_3 A	U_{z1} V	U_{z2} V	U_{z3} V	E mV	pH	T °C	η %	Comments
	0	0.51	16.95	16.5	18.6	-26	11.57	22		
	55	0.51	7.36	7.51	9.81	-537	11.80	27		
	150	0.51	5.38	5.53	6.42	-720	11.91	27		
	195	0.51	5.08	5.29	6.15	-800	12.01	27	9	Addition of indigo 0.5052 g
	240	0.51	4.73	4.88	5.63	-800	12.01	27	11	Addition of indigo 0.5039 g
I_1-I_3 individual cathode current	278	0.51	4.57	4.72	5.42	-802	11.99	27		Sample 1
cathode 1–3, $U_{z1}-U_{z3}$ cell	285	0.51	4.57	4.72	5.42	-800	11.92	27		Sample 2
voltage, E redox potential in	290	0.51	4.57	4.72	5.42	-801	11.90	27		Sample 3
catholyte, pH and temperature T ,	298	0.51	4.57	4.72	5.42	-803	11.88	27		Sample 4
η current efficiency, time of	310	0.51	4.44	4.55	5.13	-815	12.02	27		
indigo addition and dyeing										
experiments										

electrolyses higher cell voltages are observed, which decrease with duration, as ion concentration increases due to cation transport through the membrane and formation of Na-acetate from neutralisation of NaOH formed as product of the charge transport through the cation exchange membrane.

Based on the results at pH 13 the energy consumption for reduction of 1 kg of indigo can be estimated. The cell power consumption can be calculated from an upper value for the cell voltage of U_z of 6 V and a total cell current of 1.5 A with 9 W. An electrolysis time of 45 min was required to reduce an amount of 1.046 g indigo, thus for 1 kg of indigo an energy consumption of 6.5 kWh kg^{-1} is required. In an optimised system using higher current efficiency, optimised electrode geometry and higher electrolyte conductivity, an energy consumption of 2–4 kWh per kilogramme of indigo can be expected.

The theoretical consumption of dithionite and caustic soda for reduction of 1 kg of indigo is 0.664 kg $\text{Na}_2\text{S}_2\text{O}_4$ and 0.44 kg NaOH. Based on costs of \$0.08 per kilowatt hour electrical energy, the energy costs for electrochemical indigo reduction can be calculated with \$0.52 per kilogramme of indigo. The costs for chemical reduction of 1 kg indigo using $\text{Na}_2\text{S}_2\text{O}_4$ (\$0.8/kg) and NaOH (\$0.3/kg) can be calculated with \$0.66 per 1 kg indigo. In electrochemical reduction of indigo a recycling and reuse of the mediator system is possible, while use of the dithionite/caustic soda reduction leads to a considerable load of sulphate in the released effluents [1, 7, 11].

Dyeing experiments

The reduced indigo solutions were tested in dyeing experiments, to assess the electrochemically reduced indigo for possible changes in dyeing behaviour. To simulate the

Table 3 CIELab coordinates of the dyeing experiments with electrochemically reduced indigo at pH 13 and 11.8–12.0, for comparison reference dyeings also are shown

Dyebath pH	No. of dips	L^a	a^a	b^a
13	1	52.87	-5.16	-18.98
	2	46.28	-4.57	-21.99
	3	41.00	-4.31	-23.19
	4	38.99	-2.94	-25.18
11.8–12.0	1	48.75	-5.23	-21.08
	2	41.26	-3.53	-22.63
	3	35.21	-2.17	-23.64
	4	30.59	-1.17	-22.98
Reference	1% ^a	41.82	-1.89	-22.08
Reference	3% ^a	30.57	+0.40	-21.62

^a [43] % corresponds to colour depth as mass of indigo/mass of sample

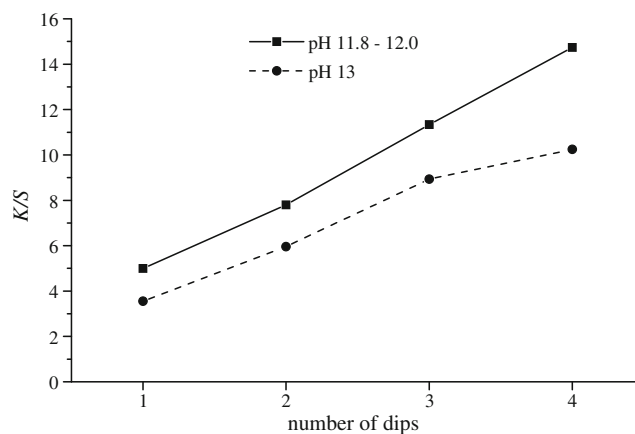
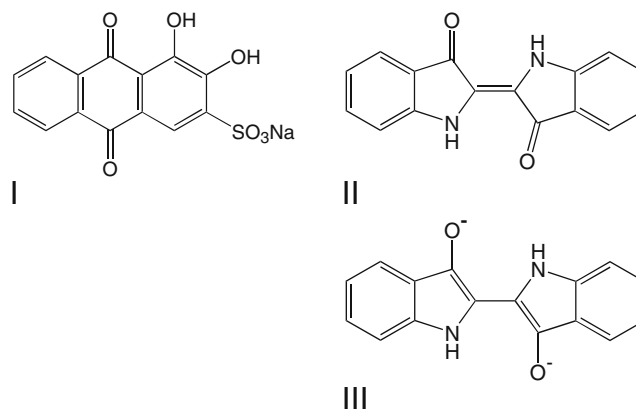


Fig. 11 Build up of K/S , measured at 660 nm as function of number of dips. Dyebath pH 13 and pH 11.8–12.0

technical indigo dyeing the build up of the colour depth was performed by repetitive immersion into the dyebath (dips) and air oxidation. The CIELab coordinates and K/S values of the indigo dyed cotton samples are presented in Table 3 and Fig. 11, respectively.

Increasing colour depth with number of dips can be recognised for both series. As expected, the presence of the mono-anion of leuco-indigo at pH 11.8 to 12.0 leads higher dyestuff uptake and darker dyeings. For comparison CIELab coordinates of reference dyeings for two different colour depths, performed with use of dithionite as reducing agent, are shown in Table 3. The two reference dyeings define the CIELab coordinates of indigo dyeings. Only small differences are observed between the electrochemical dyeings at pH 12. The colour of the four dip dyeings at pH 12 is near to the 3% reference sample and the three dip dyeings at pH 13 is similar to the 1% indigo reference. Sorption of Ca^{2+} -alizarin complex could be prevented by use of a complexing agent in the rinse bath after the dyeing. The K/S values of the experiments are shown in Fig. 11



Scheme 1 Structure of Alizarin Red S (ALS, I), indigo (II) and reduced indigo (leuco-indigo, III)

The typical pH-dependent behaviour of indigo can be recognised. Higher affinity of the indigo at pH 11.8 to 12.0 due to the presence of the mono-anion of leuco-indigo results in higher slope in Fig. 11. At pH 13 the presence of the dianion form of leuco-indigo leads to lower exhaustion during the immersion step, additionally an increasing part of already fixed, oxidised indigo becomes reduced and is removed during the following dip. Thus a lower degree of indigo fixation is observed in experiments at pH 13.

Conclusions

The electrochemical reduction and oxidation of 1,2-dihydroxy-9,10-anthraquinone-3-sulphonate (Alizarin Red S) can be observed in cyclic voltammetry. At the high pH used in this study the cathodically active form of ALS is the fully deprotonated ALS^{2-} . The indirect cathodic reduction of dispersed indigo by use of ALS can be demonstrated in CV experiments. The reduction leads to an increase of the cathodic peak current (I_p)_d attributed to the reduction of ALS^{2-} to ALS^{4-} . The formation of reduced indigo leads to an additional anodic current peak, which can be attributed to the oxidation of dissolved leuco-indigo (Scheme 1).

In voltammetry experiments in a flow cell, the plateau of the diffusion-controlled cathodic current for reduction of ALS^{2-} to ALS^{4-} at a copper cathode is observed between -850 and $-1,050$ mV. Under the experimental conditions applied, in 0.1 NaOH the height of the diffusion-controlled cathodic current density of a 5 mM ALS^{2-} solution is between 0.4 and 0.5 mA cm⁻².

Galvanostatic batch electrolysis experiments using a multi-cathode electrolyser to measure current efficiency for the indigo reduction process indicated specific energy consumption in the magnitude of 6.5 kWh kg⁻¹ of indigo. In dyeing experiments with indigo, reduced by indirect electrolysis with Alizarin Red S as mediator, it could be demonstrated that no alteration of the required indigo shade occurred. Significant optimisation of the ecologic profile of indigo dyeing processes thus can be expected from the introduction of cathodic dyestuff reduction, either for leuco-indigo production or in warp dyeing for denim production.

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